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The Action of Metals On Potassium Ferricyanide In Aqueous Solution

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THE ACTION OF METALS ON POTASSIUM FERRICYANIDE IN AQUEOUS SOLUTION

BY

RALPH ATKINSON LYNCH

THESIS

For the Degree of Bachelor of Arts

in General Science

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Ralph Atkinson Lynch

ENTITLED The Action of Metals on Potassium Ferricyanide in Aqueous Solution

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Arts in General Science

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Instructor in Charge.

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POTASSIUM FERRICYANIDE IN AQUEOUS SOLUTION.

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Previous Work.

In a paper on the action of potassium ferricyanide on metallic silver, J.M.Eder (J. pr. Chem. 16, 211(1877)) states that Schönbein (Pogg. Ann. 67, 89) had long previously observed that many metals are capable of reducing K_3FeCy_6 to K_4FeCy_6, with the simultaneous deposition of the ferrocyanide of the reducing metal on its surface. At the place cited, however, Schönbein mentions the reduction of K_3FeCy_6 by the action of light on a filter paper moistened with K_3FeCy_6 solution ;no reference is made to the action of metals on the solution, either in that paper, or in any other of the numerous papers by Schönbein published in Poggendorf's Annalen. The reference therefore appears to have been due to a misapprehension, and in so far as could be ascertained, this subject has been touched upon only by Eder himself, by G. McP. Smith, (see below) and by some one who found that K_3FeCy_6 is quantitatively reduced to K_4FeCy_6 when acted upon in aqueous solution by an excess of potassium in the form of potassium amalgam. (Roscoe and Schorlemmer's Inorganic Chemistry.)

Eder treated an excess of fairly concentrated K_3FeCy_6 solution with freshly precipitated, finely divided metallic silver for several hours in the cold. He found that that the silver changed to a brownish-white substance and that the filtered solution contained K_4FeCy_6, but that it was free from silver. The residue contained no potassium. An analysis of the solid residue by Eder gave the following results:

	Calculated.	Found.
4 Ag	67.09%	69.73%
Fe	8.69	7.96
6 Cy	24.22	——
	100.00	

Eder concludes that the residue is silver ferrocyanide; he accounts for his high result for silver by assuming that some of the silver escaped from the action through the protective influence of the deposit on its surface. Eder also determined the molecular ratio between K_4FeCy_6 in the solution, and Ag_4FeCy_6 in the residue, and found it to be exactly 3:1. He therefore deduces the equation:

$$4K_3FeCy_6 + 4Ag = 3K_4FeCy_6 + Ag_4FeCy_6.$$

In a preliminary paper on reversible metallic displacements in aqueous solutions, G.McP.Smith (J. Amer. Chem. Soc. 27, 540 (1905)) showed that upon addition of a solution of K_3FeCy_6 to mercury, an immediate action takes place, which is still more pronounced if a little potassium hydroxide is also present. In either case, a thin stiff coating, of silky, metallic lustre forms on the surface of the mercury. In the absence of alkali, a precipitate similar to Prussian blue separates; in its presence, ferric hydroxide is precipitated. The latter may be secondary product, for metallic iron gives with K_3FeCy_6 a precipitate which is apparently identical with the first, and this is decomposed by potassium hydroxide with the formation of K_4FeCy_6 and ferric hydroxide.

After the action the solution contains mercury and K_4FeCy_6.

The dissimilar results obtained in the cases of silver and mercury made it of interest to investigate the action of other metals upon potassium ferricyanide solution. The present paper is mainly qualitative, since at the start the reactions themselves were unknown, and because it is very difficult to separate many of the products in the free state. It is intended, however, to follow up the investigations quantitatively at a later date.

Experimental Part.

1. The Action of Metallic Iron.

This reaction is of fundamental importance, because the possibility is always present that some metallic iron may be displaced from the solution by another metal. In that case, the primary reaction would be accompanied by a secondary one, due to presence of metallic iron.

Of the many experiments performed, only a few will be given here.

(a) A solution of 10 grams K_3FeCy_6 in 100 cc water was heated over night on a steam bath with 3 grams of sheet iron. The filtered solution, together with K_3FeCy_6, contained K_4FeCy_6, and there was a blue deposit on the iron, which became darker upon exposure to the air. The deposit was free from potassium.

(b) In an atmosphere of hydrogen, made from zinc and dilute sulphuric acid and washed with $AgNO_3$, KOH, and water,

120 cc of water were boiled to expel the dissolved air, and then 10 grams of Kahlbaum's K_3FeCy_6 were added. The solution was heated for one-half hour in the hydrogen current; a portion was then treated with ferric alum, which gave no precipitate. 1 gram of Kahlbaum's reduced iron powder was then added, and the heating in the hydrogen current continued. Minute gas bubbles were continuously evolved from the iron, and a very faint odor of hydrocyanic acid was perceptible at the outlet. After 3 hours the iron was slightly bluish in color, and the filtered solution gave a dark blue precipitate with ferric alum, indicating the presence of K_4FeCy_6. The solution was neutral to litmus. The reaction is probably as follows:

$$4K_3FeCy_6 + 2Fe = Fe_2(FeCy_6) + 3K_4FeCy_6,$$

though it is possible that the reduction was partly brought about by the nascent hydrogen from the action of the iron on the water of the solution.

2. The Action of Metallic Silver.

The silver used in these experiments was prepared by precipitation with ferrous sulphate from a solution of silver nitrate acidified with sulphuric acid. The precipitate was washed with strong hydrochloric acid, ammonia and water, in the order named. It was dried at 150° and bottled.

The experiments of Eder were repeated, and the same results were obtained.The equation

$$4Ag + 4K_3FeCy_6 = 3K_4FeCy_6 + Ag_4FeCy_6$$

is therefore correct, provided the action be allowed to proceed at the ordinary temperature. If, however, the action was carried out at the temperature of boiling water, totally different results were obtained. Numerous experiments were performed in this case also, but a few of them will suffice to make clear the results .

(a) To 50 cc of boiling water, 5 grams of K_3FeCy_6 were added in a current of hydrogen, and to the solution 0.5 gram of finely divided silver was added. The solution almost immediately turned darker and after one-half hour a dark greenish precipitate was present. After 4 hours heating, the green substance had greatly increased in quantity, though some light colored solid was also present. The filtered solution gave no precipitate with potassium hydroxide, but gave a black precipitate with hydrogen sulphide; with hydrochloric acid, the solution gave a copious white precipitate. The solution therefore contained silver in the form of a complex salt, either $KAgCy_2$ or some other(unknown)complex cyanide, in which the silver is masked towards potassium hydroxide.

Some of the filtrate was allowed to evaporate slowly, and white crystals, which turned dark on exposure to light on filter paper were first deposited. These were not further examined, since at the time they were thought to be $KAgCy_2$. The other substances deposited from the solution were K_4FeCy_6 and a little K_3FeCy_6.

(b) To a boiling solution of 10 grams of K_3FeCy_6 in 100 cc of water, 0.4887 gram of finely divided silver was added,

in a current of hydrogen. The mixture was gently heated on a sand bath for several hours in a current of hydrogen. The clear filtered solution was acidified with dilute hydrochloric acid, and the precipitate fused with sodium carbonate. A silver button weighing 0.3630 gram was obtained.

(c) A solution made by dissolving 5 grams of K_3FeCy_6 and 3.5 grams KOH in 60 cc of water was heated over night on a steam bath with 0.504 gram of finely divided silver. Besides a little light colored residue, the flask contained a dark red precipitate, which was found to be ferric hydroxide. The filtered solution gave with hydrochloric acid a curdy white precipitate, which yielded 0.210 gram of metallic silver. The solution also contained considerable K_4FeCy_6.

It was subsequently found that Ag_4FeCy_6 is soluble to some extent in a boiling solution of K_4FeCy_6. The solution gives no precipitate with KOH; but with HCl a white precipitate, which redissolves upon addition of KOH to the mixture, is obtained. The following experiments were therefore performed:

1) A solution of 41.1 grams of K_3FeCy_6 in 150 cc of water was heated for 48 hours on a steam bath with 13.5 grams of finely divided silver. The filtered solution was acidified with dilute hydrochloric acid, and the precipitate fused with sodium carbonate. A silver button weighing 6.9210 grams was obtained.

2) A solution of 32 grams of K_4FeCy_6 in 150 cc of water was heated for 48 hours on a steam bath with 15 grams of Ag_4FeCy_6 (prepared by the precipitation of $AgNO_3$ with an

excess of K_4FeCy_6). The filtered solution was treated as in (1), and yielded a silver button weighing 5.6958 grams.

These experiments account in a very satisfactory manner for the different results obtained on treating metallic silver with cold and hot solutions of potassium ferricyanide. The primary reaction is represented by Eder's equation:

$$4Ag + 4K_3FeCy_6 = Ag_4FeCy_6 + 3K_4FeCy_6.$$

If the action takes place in the cold, no silver enters the solution. If, however, the solution is hot, the products of the primary reaction act upon each other with the formation of a complex silver salt, from which the silver is not precipitated by potassium hydroxide. This salt separates first, on evaporation, in the form of white crystals. Its nature and composition will be determined in the near future.

3. The Action of Metallic Mercury.

When a solution of potassium ferricyanide is poured upon metallic mercury, an immediate action takes place; the solution is reduced to K_4FeCy_6, and mercury simultaneously enters the solution. Mercury is still more readily dissolved if potassium hydroxide is also present. In the absence of alkali, a precipitate similar to Prussian blue separates; in its presence ferric hydroxide is formed. The latter may be considered as a secondary product, since the blue precipitate is decomposed by KOH into K_4FeCy_6 and $Fe(OH)_3$. The most interesting phenomenon accompanying the reaction is that, whether KOH be added or not, a thin, stiff coating of silky, metallic

luster at first forms on the surface of the mercury. If a little of this is at once removed and washed with dilute KOH solution, and then with water, and the product is ignited on platinum foil, a slight residue is left, which possesses magnetic properties. It would therefore appear that the primary reaction is represented by the equation:

$$2K_3FeCy_6 + 3Hg = 3K_2HgCy_4 + 2Fe.$$

The reaction may then become more complex, owing to the presence of metallic iron, as follows:

$$4K_3FeCy_6 + 2Fe = 3K_4FeCy_6 + Fe_2FeCy_6,$$

and in case KOH is also present, we have,

$$Fe_2FeCy_6 + 4KOH = 2Fe(OH)_2 + K_4FeCy_6$$

$$\text{and } 2Fe(OH)_2 + 2K_3FeCy_6 + 2KOH = 2Fe(OH)_3 + 2K_4FeCy_6$$

(Skraup, Ann. 186, 385f). The entire action, therefore can possibly be summed up as follows:

$$8K_3FeCy_6 + 3Hg + 6KOH = 6K_4FeCy_6 + 3K_2HgCy_4 + 2Fe(OH)_3.$$

A. Experiments performed in the absence of alkali.

To a boiling solution of 6.58 grams of K_3FeCy_6(Kahlbaum's) contained in an Erlermeyer flask, a large excess (50 grams) of mercury was added, and the mixture was gently heated on a sand bath for 5 hours in a current of hydrogen. The solution was then filtered and the mercury determined as HgS, of which 0.5095 gram (equivalent to 0.4318 gram Hg) was obtained.

On treating a solution of 3.00 grams of K_3FeCy_6 in the cold for 4 days with an excess of mercury, Smith (loc. cit.) obtained 0.2358 gram of HgS from the solution. On comparing

this with the above result, we get the proportion:

$$3 : 6.58 = 0.2358 : x; \qquad x = 0.5171 \text{ gram HgS},$$

a figure which agrees very closely with 0.5095.

On comparing these results with the equations,

$$\begin{array}{l} 2K_3FeCy_6 + 3Hg = 3K_2HgCy_4 + (2Fe) \\ 4K_3FeCy_6 + (2Fe) = 3K_4FeCy_6 + Fe_2FeCy_6 \\ \hline 6K_3FeCy_6 + 3Hg = 3K_2HgCy_4 + 3K_4FeCy_6 + Fe_2FeCy_6, \end{array}$$

we see that 6.58 grams of K_3FeCy_6 dissolves only 0.4318 instead of 2 grams of mercury. The reaction therefore does not proceed quantitatively according to the above equation.

B. Experiments performed in the presence of alkali.

50 grams of mercury were allowed to stand for two weeks, with occasional shaking, with a solution of 6.5800 grams of K_3FeCy_6 and 0.85 gram KOH (both of Kahlbaum's manufacture), in a stoppered Erlenmeyer flask at the ordinary temperature. The mercury immediately became coated with iron amalgam, and at first the action was very rapid, especially on shaking. The dark red precipitate of $Fe(OH)_3$ gradually appeared and accumulated, the amalgam became dull and dirty, and a great deal of finely divided mercury formed. After 5 days, the mercury had mostly gathered together again into one mass, and no further action was apparent, even on shaking. The solution was still weakly alkaline.

The mercury was precipitated from the boiling hot solution with hydrogen sulphide, and the precipitate collected in a Gooch crucible. The filtrate from the HgS was tested and

found to contain no more mercury. After washing with carbon disulphide, the HgS weighed 1.8943 grams (equivalent to 1.6330 grams Hg). This is the last and certainly the most accurate of three experiments which were performed. The first gave 1.6970 grams and the second 1.5080 grams of dissolved mercury, but errors are known to have been made in these two determinations. In the third experiment, advantage was taken of the previous experiences, and the determination is considered very accurate.

According to the equation worked out above for this case, 6.58 grams of K_3FeCy_6 and 0.841 gram KOH should dissolve only 1.4973 grams Hg, and, unless the reaction is more complicated than was at first supposed, it is difficult to account for the excess (9.06 %) of mercury dissolved.

Another reaction is however possible in the present case, for potassium ferricyanide, in alkaline solution, is a strong oxidizing agent. Furthermore, most complex cyanides are decomposed more or less readily by mercuric oxide, e.g.,

$$K_2NiCy_4 + 2HgO + 2H_2O = Ni(OH)_2 + 2KOH + 2HgCy_2.$$

(On this reaction depends Liebig's method for the separation of nickel and cobalt; K_3CoCy_6 is not decomposed by mercuric oxide.) The action of mercuric oxide upon K_3FeCy_6 solution was investigated, and it was found that the salt is readily decomposed, even by the red oxide and in the cold,- essentially according to the equation,

$$K_3FeCy_6 + 3HgO + 3H_2O = Fe(OH)_3 + 3KOH + 3HgCy_2.$$

A slight excess of K_3FeCy_6 was used in concentrated solution,

and ferric hydroxide was obtained, which was entirely free of HgO. A white, crystalline substance crystallized out, which appeared to be mercuric cyanide. The original filtrate from the $Fe(OH)_3$ and $HgCy_2$, however, appeared to contain some K_4FeCy_6, since it gave a dark blue precipitate with ferric alum.

Assuming that the reaction between the metallic mercury and the ferricyanide solution took place according to this second possible process, we may deduce the final equation as follows:

$$\begin{array}{rcl} (2K_3FeCy_6 + 2KOH & = & 2K_4FeCy_6 + H_2O + O\ ) \times 3 \\ (\ Hg + O & = & HgO\ ) \times 3 \\ K_3FeCy_6 + 3HgO + 3H_2O & = & Fe(OH)_3 + 3KOH + 3HgCy_2 \\ \hline \end{array}$$

$$7K_3FeCy_6 + 3KOH + 3Hg = 6K_4FeCy_6 + Fe(OH)_3 + 3HgCy_2.$$

According to this equation, 6.58 grams of K_3FeCy_6 should dissolve 1.7112 grams of mercury. This, in turn, is a higher result (by 4.79 %) than was obtained; and strange to say, the actual result obtained is almost the exact mean of the theoretical results of the two processes.

a) 1.4973
mean = 1.6042; result obtained = 1.6330.
b) 1.7112

It appears then, that both of the possible reactions actually do take place simultaneously. The first is known to take place, because iron amalgam is formed in sufficient quantity to be distinguished by the naked eye; and the second must take place also, because more mercury is dissolved than is possible according to the first reaction.

C. Experiments in the presence of hydrochloric acid.

After having completed the foregoing experiments in neutral and alkaline solutions, the action of mercury was tried upon an acidified solution of K_3FeCy_6--10 cc of mercury were placed in each of three beakers, which contained 25 cc of water, 25 cc of 5% KOH-solution, and 25 cc of 5% hydrochloric acid respectively. To each solution 5 cc of moderately concentrated K_3FeCy_6-solution were added, and the actions observed and compared. The coating on the mercury was formed in all three cases, most rapidly in the acid, and least rapidly in the alkaline solution. After a short time the acid liquid and the free-flowing mercury were decanted, and the stiff mercury residue was washed several times by decantation with water, then with KOH-solution to remove any insoluble complex cyanide adhering to the mercury, and finally with water. The product was ignited to drive off the mercury, and a minute residue remained which was attracted by a magnet.

The results indicate that in all three cases, metallic iron actually is deposited from the solution. The deposit is, however, only transitory,-since the iron is further acted upon by the solution, and its separation takes place more readily in acid than in alkaline solution.

4. The Action of Metallic Nickel.

(a) 30 grams of Kahlbaum's electrolytic nickel were heated for three days on a steam bath with a solution of 10 grams of K_3FeCy_6 in 100 cc of water. The nickel was coated with a

loosely adhering greenish-blue deposit, which rendered filtration very difficult. After five or six filtrations, a clear solution was obtained which was found to be largely reduced to K_4FeCy_6.

(b) 23 grams of nickel were allowed to stand for 5 weeks at the ordinary temperature, in a stoppered flask, with a solution of 6.58 grams of K_3FeCy_6 in 100 cc of water. The nickel was coated with a heavy, greenish deposit, which very readily ran through the filter. The filtrate was boiled and filtered twice before it was obtained clear. The greenish-yellow liquid contained no nickel, and consisted mainly of K_4FeCy_6.

In the presence of potassium hydroxide, the same results were obtained, though the liquid was readily filtered. The solution contained no nickel. The reaction is probably the following:

$$4K_3FeCy_6 + 2Ni = Ni_2FeCy_6 + 3K_4FeCy_6.$$

5. The Action of Metallic Zinc.

25 grams of pure zinc were treated for one month with a solution of 6.58 grams of K_3FeCy_6 in 100 cc of water. At the end of that time, a dark, greenish precipitate was present, besides the excess of zinc. The solution was boiled and filtered twice before it could be obtained clear. It was then allowed to crystallize, upon which crystals of both K_4FeCy_6 and K_3FeCy_6 appeared. The substances were redissolved, and the solution tested for zinc as follows:

A considerable portion was evaporated with 2 cc of con-

centrated sulphuric acid, and the excess of acid fumed off. The residue was dissolved in water, and the iron oxidized by boiling with nitric acid. The iron was then precipitated from the hot solution with an excess of ammonia, and the filtrate weakly acidified with acetic acid. Hydrogen sulphide was passed in and a very slight white precipitate formed which appeared to be sulphur, proving the absence of zinc in the solution. The reaction is probably represented by the following equation:

$$2Zn + 4K_3FeCy_6 = Zn_2FeCy_6 + 3K_4FeCy_6.$$

6. The Action of Metallic Gold.

(a) A solution of 2 grams of K_3FeCy_6 in 25 cc of water was treated for two weeks in a stoppered flask with 0.1555 gram of pure gold (precipitated with oxalic acid). It was then heated for 5 hours on a steam bath, and finally allowed to stand for three weeks longer at the ordinary temperature. The solution was filtered from a blue deposit and the excess of gold, and electrolyzed with a silver cathode. A deposit of gold formed on the cathode, showing that some gold entered the solution.

(b) An equal quantity of the same solution was treated in exactly the same way with 0.1780 gram of gold, in the presence of 0.06 gram KOH. It was then filtered and electrolyzed as above with the same result.

7. The Action of Silver Oxide.

After having found that mercuric oxide acts readily upon K_3FeCy_6 in aqueous solution, it was suggested to try the action

of silver oxide upon the same solution. With that end in view, about 1 gram of the freshly precipitated oxide was added to an excess of K_3FeCy_6-solution. A reaction immediately set in, which continued for several hours; the solution was rapidly reduced to K_4FeCy_6. The silver oxide changed in color from brown to jet black, and a gas was gradually evolved, which was found to be oxygen. The black solid gave upon addition of nitric acid a reddish-orange product, insoluble in nitric acid, which was found to be identical with Ag_3FeCy_6. The following reactions are proposed to account for the phenomena observed:

$$K_3FeCy_6 + 3AgOH = Ag_3FeCy_6 + 3KOH,$$

$$4Ag_3FeCy_6 + 4AgOH = 4Ag_4FeCy_6 + 2H_2O + O_2.$$

Silver ferricyanide is colored jet black by KOH-solution, and the original color is again restored by the addition of nitric acid in excess. Silver ferrocyanide is also oxidized by nitric acid to the ferricyanide. It is therefore seen that the above reactions account, qualitatively at least, for all the phenomena observed. It is possible that the black body formed in the present case is the unstable peroxide of silver. After having stood for several weeks under the reaction mixture, the solid residue consisted of two layers. The top layer was orange-red in color (Ag_3FeCy_6) and the bottom layer was white (Ag_4FeCy_6).

It is intended later to investigate the properties of the mixture as an oxidizing agent for organic compounds. The indications are that it will be found more active than the ordinary alkaline ferricyanide mixture.

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